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Portable Vacuum X-Ray Spectrometer Instrument for On-site Analysis of Airborne Particulate Sulfur and Other Elements

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Interagency Energy/Environment R&D Program Report

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by

J. V. Gilfrich
L. S. Birks

Naval Research Laboratory
Washington, D. C. 20375

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Project Officer

Jack Wagman, Director
Emissions Measurement and Characterization Division
Environmental Sciences Research Laboratory
Research Triangle Park, North Carolina 27711

ENVIRONMENTAL SCIENCES RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U. S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, N. C. 27711

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ABSTRACT

A portable vacuum wavelength-dispersive x-ray analyzer has been constructed for on-site measurements of the sulfur content of filter-deposited airborne particles. Although designed to analyze for sulfur, the spectrometer is adjustable over a limited range providing the potential for determining other elements. With the x-ray tube rated at 50 watts, the instrument achieves a 100-second 3σ detection limit for sulfur of better than 0.5 $\mu g/cm^2$.

INTRODUCTION

The use of x-ray fluorescence analysis for the measurement of the elemental composition of the particulate material filtered from source emissions or from the ambient air or water has become a well-established technique (1-3). Commercial instrumentation, both wavelength-dispersive and energy-dispersive, is available which can provide the laboratory with the capability of providing rapid, low-cost and accurate results (1-5). This laboratory equipment, however, is expensive and bulky, making it inconvient for transporting to an emission source for on-site measurements. Previously (6), the Naval Research Laboratory (NRL) constructed for the Environmental Protection Agency (EPA) a compact x-ray analyzer which could perform on-site analyses. Because it was an air path instrument it was limited to measuring elements above atomic number 23 (V).

Concern for the pollution caused by the emissions from combustion sources has been magnified recently by the increasing need to use the less-desirable supplies of fossil fuels (i.e. high sulfur coal and high vanadium oil) for energy production. In view of the resultant higher levels of primary sulfates produced (7), the EPA asked NRL to construct a second-generation portable x-ray analyzer specifically to analyze for sulfur in particulate emissions from such sources. The goal was to achieve a 3σ detection limit (8) of 5 $\mu g/cm^2$ in 100 seconds. Although a fixed spectrometer would be adequate to measure sulfur alone, the versatility provided by an adjustable spectrometer suggested that the instrument should be able to cover some range of 2θ angle. The purpose of this report is to document the construction and suggest operating parameters for this instrument.

INSTRUMENT DESIGN

As in the previous case (6) it was not the intent of the work reported here to conduct research in the area of crystal spectrometer design. Rather it was felt that commercially available state-of-the-art components could be used with minimum modification so that specially fabricated parts would be few. In addition to the detection limit criterion (above), the specifications called for 1.) light weight, 2.) only 120 volt A.C. power (no water or liquid nitrogen), and 3.) sufficient resolution to minimize interference particularly from Pb M-lines when measuring S K-lines.

In accordance with the specifications and design criteria discussed above the instrument was optimized for the measurement of S Kα by employing an air-cooled 50-watt Pd transmission-target x-ray tube, a cleaved NaCl crystal and a Ne-CO_2 sealed proportional detector. The Pd L-lines are particularly effective for exciting the S K-spectrum (Pd Lα-4.37Å, Pd Lβ-4.15Å; S K edge-5.02Å); with the target material deposited on the inner surface of the Be window, the transmission geometry permits close coupling to the sample. The NaCl crystal was chosen because its interplanar spacing (2d = 5.64Å) diffracts S Kα radiation (λ = 5.37Å) to a high Bragg angle ($\theta = 72^{\circ}$) giving the best dispersion for minimum interference from neighboring lines. The crystal is used with a cleaved surface to produce a narrow diffraction profile and when coupled to a fine collimator (4" x 0.005") provides a resolution of about 3 eV (0.007Å) at S Kα. For the Ne detector used, 63% of the S Kα radiation is transmitted by the Be window and 98% of that is absorbed by the Ne gas. Figure 1 is a block diagram of the Sulfur Analyzer and Table 1 lists the components in detail separating those commercially available and their cost from those fabricated at NRL, with our best estimate of what the latter would cost if available from commercial sources. Figure 2 is a photograph of the instrument.

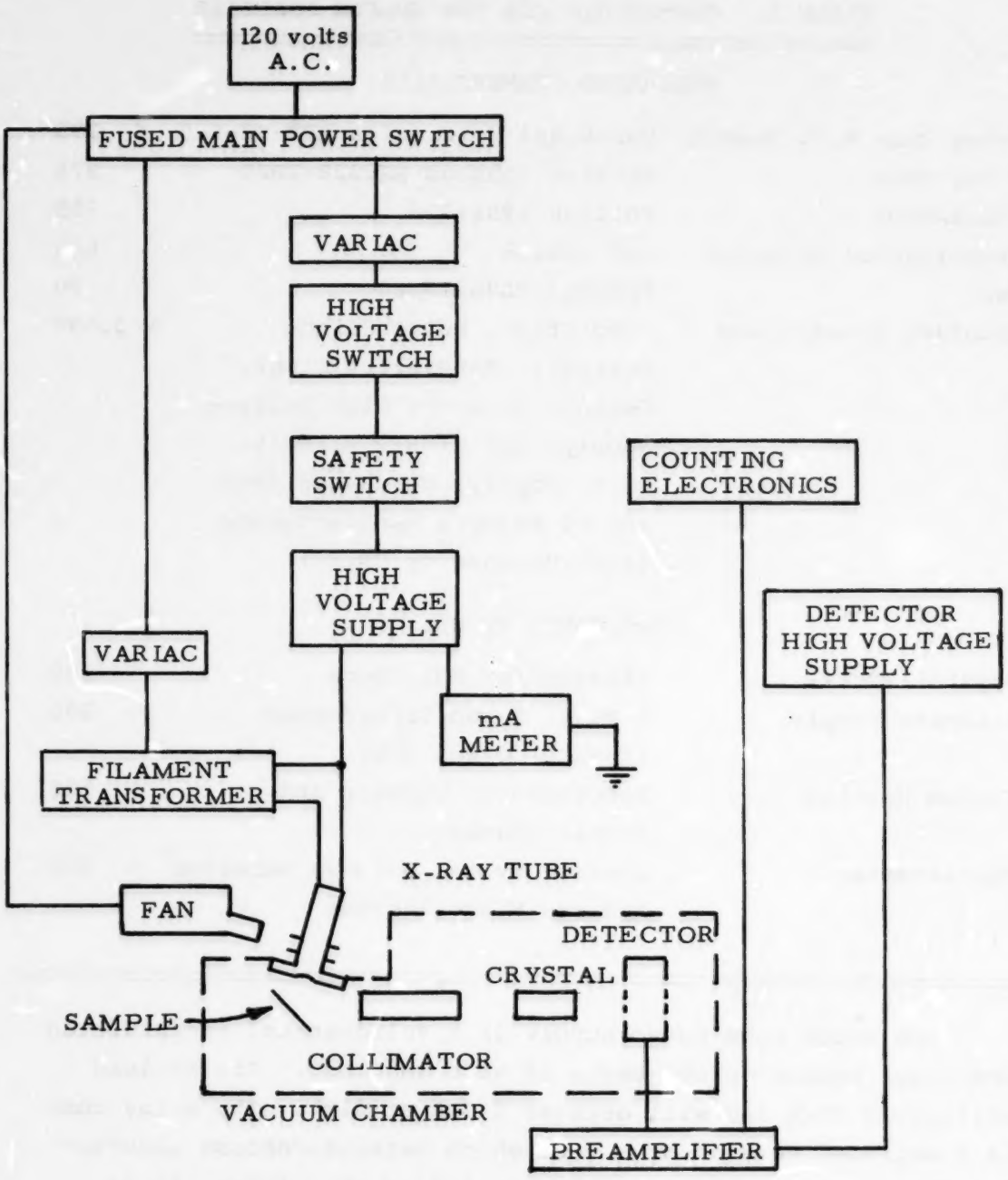

Figure 1. Block Diagram of the X-Ray Analyzer.

TABLE 1. COMPONENTS FOR THE SULFUR ANALYZER

PURCHASED COMMERCIALLY

X-Ray Tube H.V. Supply	Universal Voltronics BPE-32-5.5	$ 295
X-Ray Tube	Watkins-Johnson WJ2328-2DPD	975
Collimator	Philips 19011200	255
Proportional Detector	LND 42513A	600
Fan	PAMOTOR RL90-18/00	20
Counting Electronics	(Amplifier, Pulse Height Analyzer, Ratemeter, Timer, Scaler, Detector High Voltage Supply, and NIMBIN with its Power Supply) purchased from any of several manufacturers (e.g. Harshaw or ORTEC)	∿ 3,000

FABRICATED AT NRL

Crystal (NaCl)	Cleaved for NRL Stock	∿ 100
Filament Supply	5 volt, 5 amp Transformer (insulated for 50kV)	∿ 200
Vacuum Housing	Spectrometer Chamber and Sample Chamber	∿ 500
Spectrometer	Gears, Crystal Holder, Detector Arm and Miscellaneous	∿ 500

The x-ray tube power supply is a solid-state, encapsulated component chosen on the basis of size and cost. Its no-load voltage is 36kV and will deliver 5.5mA at 32kV. The x-ray tube is a modified version of a tube which Watkins-Johnson manufactures (9). Since the anode is mounted to the window, it is grounded, requiring that the filament transformer be insulated for the high voltage. The detector is a modified version of a catalog item from LND.

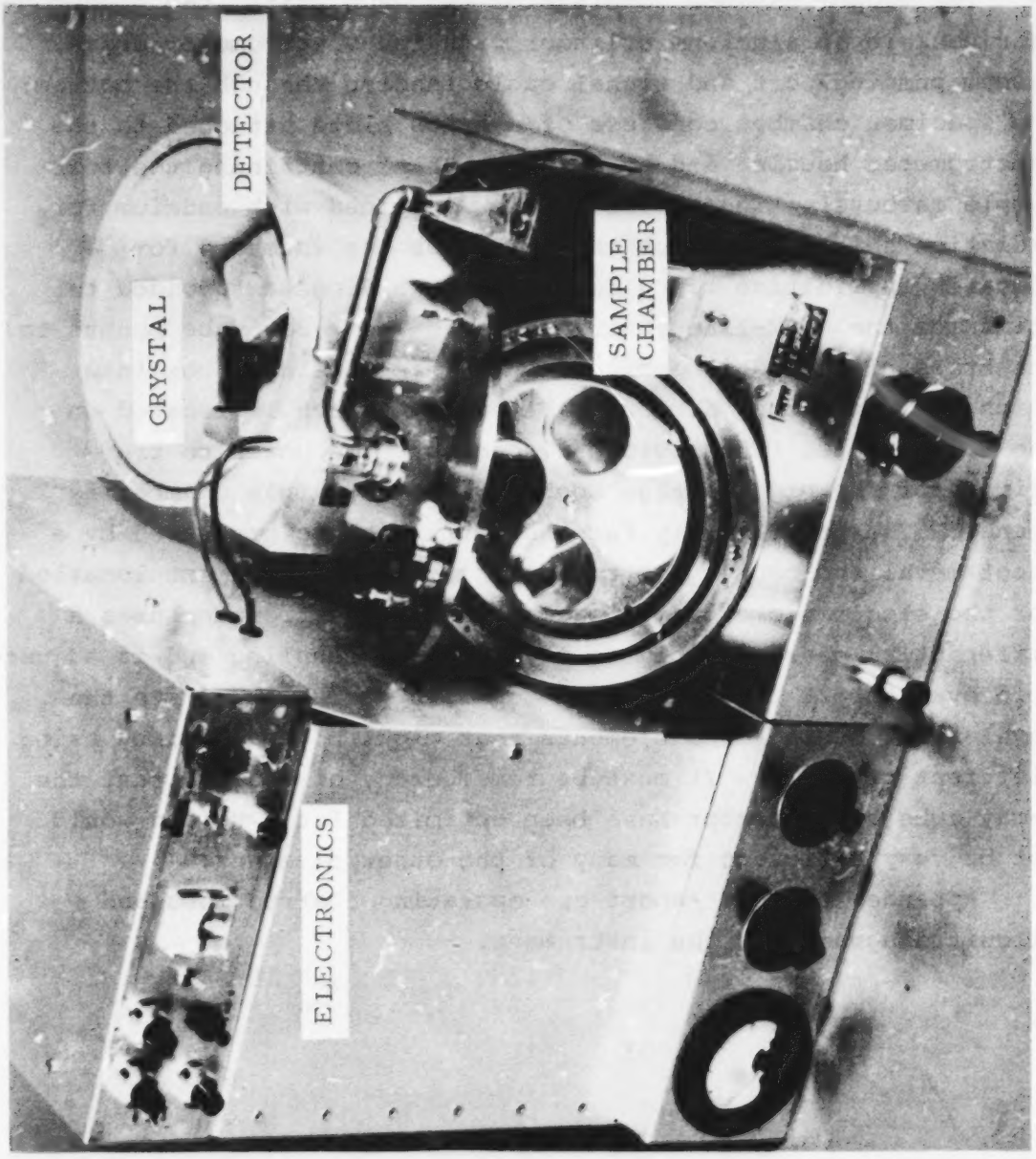

Figure 2. Photograph of the X-Ray Analyzer. Sample chamber is open. The top of the spectrometer vacuum tank and the shielding for the x-ray tube have been removed to show some detail.

The vacuum chamber consists of two main units: the spectrometer tank is an aluminum cylinder with the spectrometer drive, vacuum pumping port and signal cable feeding through the bottom; the specimen chamber consists of a brass plate attached to the spectrometer housing and an aluminum "hat" containing the four-sample carousel. The sample chamber is lined with cadmium for radiation shielding (since the prototype was intended for specific application to sulfur, lead shielding was avoided to eliminate the Pb M-line interference). The x-ray tube mounts to the brass plate and is enclosed by a lead-shielding box into which cooling air is directed. A safety switch is located on the brass plate. This switch disconnects the power to the primary of the high voltage supply when the sample chamber is opened. The power supply for the x-ray tube is protected by a sheet metal enclosure, the top of which is a convenient location for the electronic counting package. The spectrometer uses a differential gear assembly to provide θ-2θ coupling and is adjustable over the 2θ range of $\sim 90^{\circ}$ to $\sim 150^{\circ}$. Table 2 lists the wavelength coverage and elements that might be analyzed by using different crystals. It must be remembered, of course, that the x-ray tube and detector have been optimized for S Kα and would not be very efficient for many of the other elements.

Appended to this report are operating instructions and circuit diagrams for the instrument.

TABLE 2. POSSIBLE RANGE FOR THE SPECTROMETER
(2 FROM 90° TO 150°)

Crystal	2d (Å)	Min.λ (Å)	Max.λ (Å)	Element Kα	Element Lα
LiF (220)	2.85	2.01	2.75	Mn-Ti	Ba-Gd
LiF (200)	4.03	2.85	3.89	Sc-K	In-Cs
NaCl	5.64	3.99	5.45	Ar-S	Mo-Ag
Graphite	6.71	4.74	6.48	S-P	Y-Ru
PET	8.75	6.19	8.45	Si-Al	Br-Y
ADP	10.6	7.50	10.2	Al-Mg	As-Kr
Gypsum	15.2	10.7	14.7	Na-Ne	Ni-Ga
Mica	19.9	14.1	19.2	Ne-F	Fe-Ni
Acid Phthalate (K, Rb or Tl)	∿ 26	∿ 18	∿ 25	F-O	V-Mn

RESULTS

The sensitivity and detection limits were measured on a sample of CdS deposited on a Millipore filter. The mass loading of CdS was measured by analyzing for both Cd and S on the multi-spectrometer x-ray fluorescence analyzer at the EPA laboratory in Research Triangle Park, N. C. The standards used for these measurements were films of CuS and CdF_2 on mylar obtained from MicroMatter Co., Seattle, Wash. The results of these measurements showed 114 $\mu gCd/cm^2$ and 32.8 $\mu gS/cm^2$, values agreeing with stoichiometry within 1%. With the x-ray tube in this sulfur analyzer operated at 30 kV and 1.5 mA, the average of several determinations of S Kα intensity gave a value of 2935 c/100s (σ = 40 c/100s for 10 meas.) for the sulfur in the CdS sample, above a background of 177 c/100s. This results in a sensitivity of 89.5 $c/100s/\mu g/cm^2$ for sulfur and a 100 second detection limit of $\frac{3\sqrt{177}}{89.5} = 0.45\ \mu g/cm^2$, about one order of magnitude better than the design criterion.

Because of the success experienced with the NRL laboratory x-ray analyzer in distinguishing between the sulfide and sulfate forms of sulfur (10), an attempt was made to measure the S Kβ spectrum in this instrument. Using a bulk sample of either $Na_2\ SO_4$ or elemental S and operating the x-ray tube at 30 kV, 1.5 mA, no signal above background could be observed in the region of the S Kβ line. The anticipation that this low-power sulfur analyzer might be able to distinguish between the sulfide and sulfate could not be realized. The use of a higher power x-ray tube could upgrade the instrument to a degree that such measurements might be made. There are two reasons which argue against the practical success of such a modification: 1.) Significantly higher powered tubes (> 10X) would certainly have to be water cooled and require a much larger x-ray tube power supply, making

the instrument much less portable, if it could be called portable at all; and 2.) Moderately higher power tubes (4 or 5x) might still be air-cooled, but would certainly be larger in size making it unlikely that the tube target to sample coupling could be nearly as close (an increase in sample to target distance of a factor of 2 would require a power increase of a factor of 4 just to maintain the same capability).

SUMMARY

The low-powered portable sulfur x-ray analyzer constructed by NRL for EPA has demonstrated a 100 second 3σ detection limit of about 0.5 μg/cm^2 for sulfur in particulate samples collected on Millipore filters. It is a wavelength-dispersive instrument having a resolution of about 3 eV (0.007Å) at the S Kα line. It is portable, requiring only 120 volt, 60 Hertz A.C. power and is contained in three packages: the main chassis, containing the spectrometer, sample chamber and x-ray tube power supply; the electronic counting equipment; and the vacuum pump.

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APPENDIX

The instrument described in this report is in most ways a conventional, manual wavelength-dispersive x-ray fluorescence analyzer. As such, its operation is very straightforward for anyone familiar with that type of equipment. However, the details of operation are included here to assist with the specific steps required to provide for most efficient use of the instrument. Also included in this Appendix are the details of the circuitry, along with circuit diagrams as an aid if trouble-shooting should become necessary.

OPERATION

Referring back to Figure 2, the controls on the base of the instrument include the ON-OFF switch, the high voltage switch (not shown), the high voltage adjust and tube current adjust knobs, and the 2θ adjust crank. Along with the dial to indicate the 2θ angle and the meter to read tube current, these controls are used to turn the instrument on and set the spectrometer. Operation of the instrument can best be illustrated as a series of steps consisting of

1. Evacuating the spectrometer
2. Initial setting of electronics
3. Turning on x-rays
4. Setting counting circuit parameters
5. Measuring samples

Each of these steps will be treated in some detail.

Initially, it should be ascertained that the preamplifier, located immediately below the spectrometer tank is connected properly, i.e. the signal cable coming out of the bottom of the tank is connected to the input of the preamp, and that the preamp power cable, the detector high voltage cable and a signal cable are attached to the appropriate connectors at both the preamp end and the counting electronics end. Figure A-1 is a block diagram of the counting electronics to illustrate proper connections. This x-ray spectrometer is intended to be used with a conventional set of NIMBIN counting electronics such as is available from a myriad of manufacturers.

1. Evacuating the spectrometer: with the vacuum pump connected to the copper tubing through the hole in the right side of the chassis, the NaCl crystal is placed in the crystal holder and the lid put on the chamber. Samples and appropriate blanks and standards are put in the sample carrousel and the sample chamber closed. Vacuum pump is turned on. If monitoring of the vacuum condition is desired, the appropriate control box for the thermocouple gauge is attached to the gauge mounted in the spectrometer lid; otherwise the sound of the vacuum pump can be used to estimate the condition of the vacuum. (The thermocouple gauge used is a CVCGTC-004 or its equivalent; an appropriate control box would be the CVCGTC-100.)

2. Initial setting of the electronics: with a standard containing 30-50 $\mu gS/cm^2$ in the sample chamber, the spectrometer set for 145° 2θ (SKα with NaCl crystal) and the vacuum chamber pumped down, set the electronics as follows: Pulse height analyzer-Int. Diff switch in Int position, E at 1.00, ΔE at 0.50; amplifier gain at the high end of its range; ratemeter range switch at most sensitive position; timer set to maximum time; and detector high voltage set to +1100 volts. Turn on power to the counting circuits and reset and start the scaler. Adjust the "E" dial on the pulse height analyzer so that it is set just high emough to eliminate electronic noise (x-rays should <u>not</u> be turned on at this

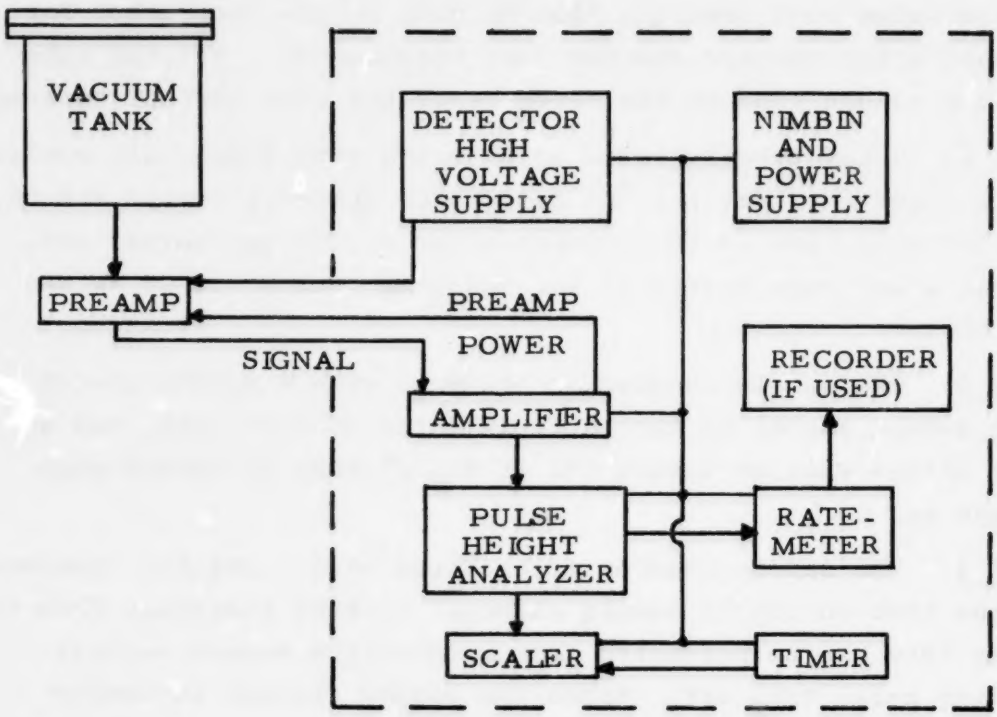

Figure A-1. Block Diagram of Counting Electronics. (Components inside dashed lines obtained commercially.)

stage.) When making this adjustment, it is probably more convenient to observe the scaler readout rather than the ratemeter to determine the "E" setting at which the onset of noise occurs.

3. Turning on x-rays: Main on-off switch is turned on. Check to be sure fan is operating. Turn on high voltage switch. Increase high voltage adjust knob to some moderate values (say 20 on the dial). Increase tube current adjust to achieve some small reading on the meter. Set the high voltage adjust knob to the value read from the plot mounted on the instrument for the operating voltage desired (see Figure A-2). Set the tube current adjust knob so the meter reads the tube current desired.

NOTE 1: X-ray tube is rated at 50 watts with forced air cooling. It is important that the fan be running whenever x-rays are on, and for some time (≈ 10 minutes) after x-rays are turned off. Normal x-ray tube operation for measuring sulfur is 30 kV and 1.5 mA.

NOTE 2: The sample chamber is equipped with a safety switch so that x-rays cannot be turned on with the chamber open, and so that x-rays will be turned off if the chamber is opened when x-rays are on.

NOTE 3: The sample chamber is equipped with a shutter (operated by the knob on top of sample chamber) so that radiation from the x-ray tube can be prevented from reaching the sample without turning x-ray tube off. Since the sample chamber is vacuum pumped through this opening, it is important that the shutter be open during pump down. If it is closed, it will be difficult or impossible to open it (and sample chamber will not be pumped efficiently). If a safety switch could be mounted so that it was actuated when the shutter was closed, and was wired in parallel with the other safety switch, the sample chamber could be opened with the shutter closed without turning off the x-rays, assuming that the shutter is radiation-safe. This last point would have to be confirmed.

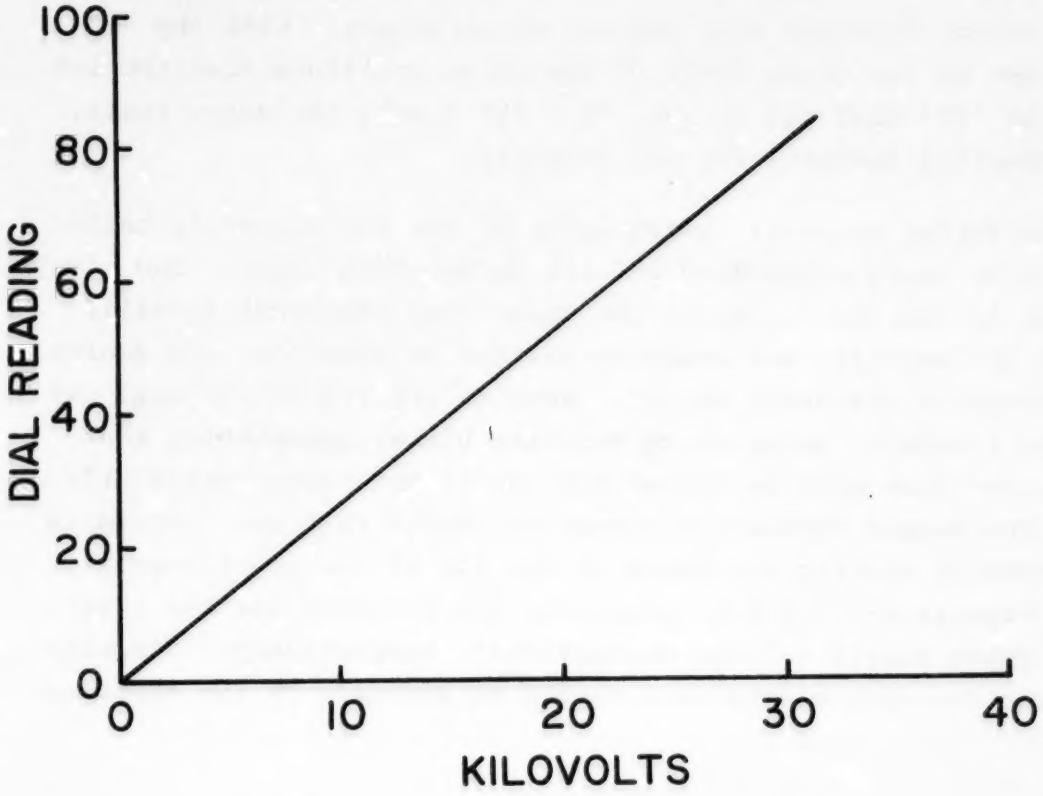

Figure A-2. X-Ray Tube High Voltage as a function of the Dial Reading.

4. Setting counting circuit parameters: with the x-rays on and set to 30 kV and 1.5 mA, adjust the 2θ dial to achieve maximum intensity. Change the Int.-Diff. switch to Diff. and measure the pulse amplitude distribution of the S Kα radiation by varying the "E" dial. The peak of the pulse amplitude distribution can be varied by changing the amplifier gain or the detector high voltage. A convenient value for the peak is 3 volts on the "E" dial. This can be achieved by varying amplifier gain and/or detector high voltage as necessary. With the "E" dial set at the lower limit of the pulse amplitude distribution and the "ΔE" dial set so that "E + ΔE" equals the upper limit, the counting circuits are set properly.

5. Measuring samples: Sensitivity of the instrument is calibrated by using a standard and its appropriate blank. The timer switch is changed to one of the fixed time positions (usually 10 or 100 seconds) and counting started by resetting the scaler and pressing the start switch. Samples are run in the same way as the standard, using an appropriate blank, remembering that the x-ray tube must be turned off (or it will turn itself off) when the sample chamber is opened to change samples. Vacuum is released by opening the valve on the lid of the spectrometer.

Figures A-3 and A-4 illustrate the circuits for the x-ray tube power supply and the preamplifier, respectively. Circuits for the counting electronics should be provided by the supplier.

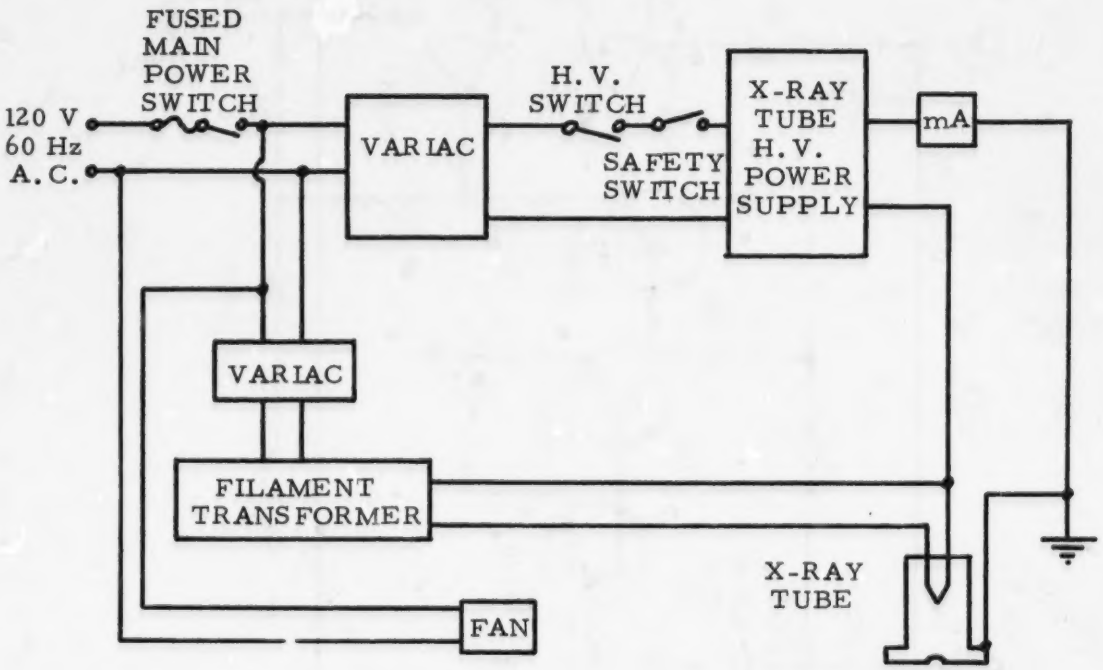

Figure A-3. Block Diagram of the Main Power Circuit.

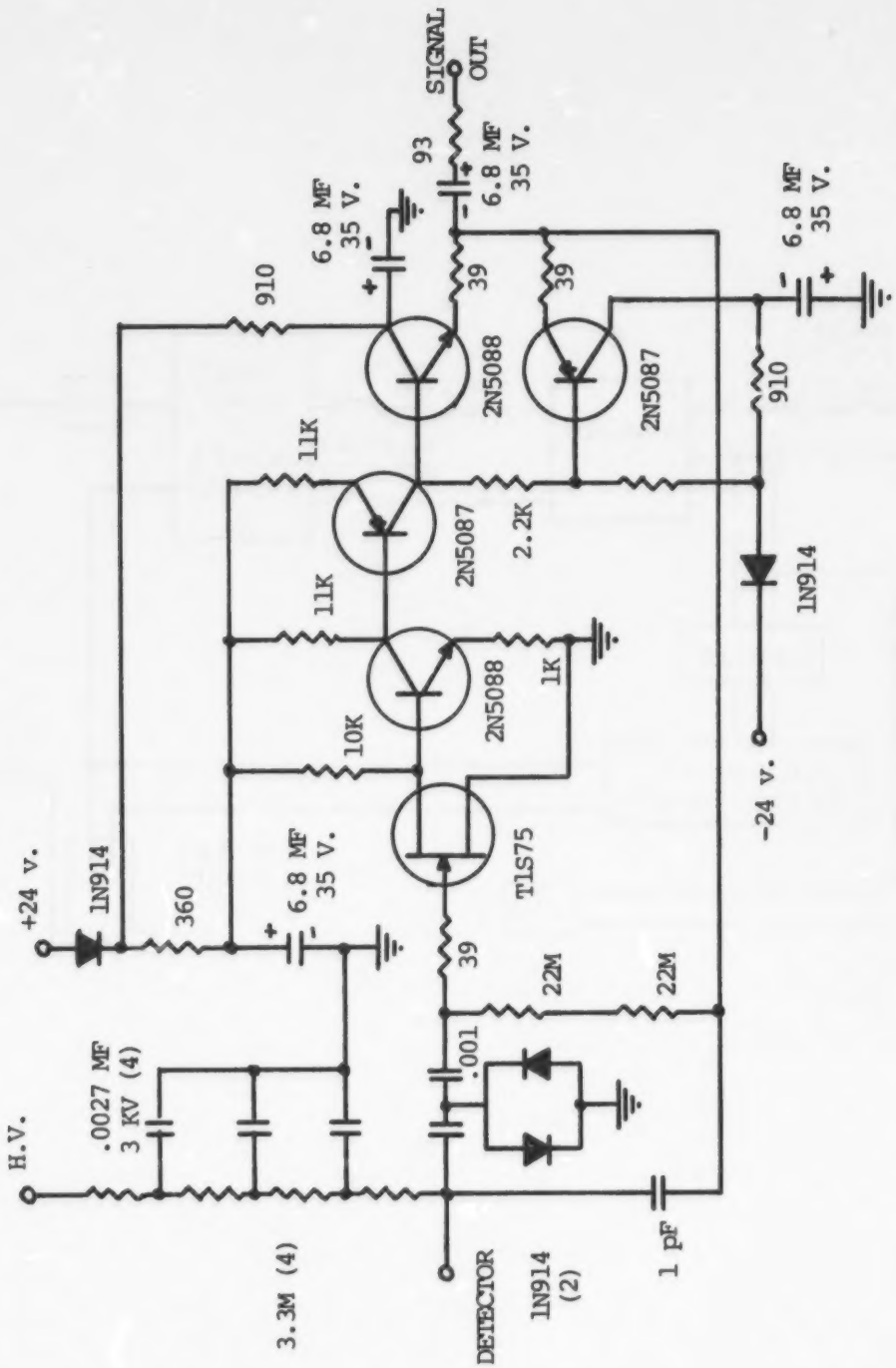

Figure A-4. Schematic Diagram of the Preamplifier